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OKLAHOMA UNIV NORMAN DEPT OF CHEMISTRY

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THE X-RAY CRYSTAL STRUCTURE OF TRIMETHYLTIN (IV) AZIDE. A UNIQUE--ETC(U)

SEP 79 D CUNNINGHAM , M B HOSSAIN

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The X-Ray Crystal Structure of Trimethyltin(IV) Azide. A Unique
One-Dimensional $\{[(CH_3)_3Sn]^{\delta+}[(CH_3)_3Sn(N_3)_2]^{\delta-}\}_n$ Polymer

by

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STATEMENT

Our 1978 review of the tin structural literature (ref. 11) reveals many examples of axially-most-electronegative, trigonal bipyramidal triorganotin moieties in associated polymer chains, but the structure of trimethyltin azide is unique in consisting of SnC_3 moieties in alternating $[(\text{CH}_3)_3\text{Sn}]^{\delta+}$ cationic and $[\text{N}_3(\text{CH}_3)_3\text{SnN}_3]^{\delta-}$ anionic environments in a one-dimensional array with the tin atoms bridged at unequal distances by the α -nitrogen atoms of the azide group at which site the chains are bent.

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The X-Ray Crystal Structure of Trimethyltin(IV) Azide at 138K. A Unique,
One-Dimensional $\{[(\text{CH}_3)_3\text{Sn}]^{\delta+}[(\text{CH}_3)_3\text{Sn}(\text{N}_3)_2]^{\delta-}\}_n$ Polymer

By Desmond Cunningham⁺, M. B. Hossain, K. C. Molloy, D. van der Helm* and J. J. Zuckerman*

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Summary

The structure of trimethyltin(IV) azide, as determined at 138K by X-ray diffraction, consists of one-dimensional polymeric chains in which planar SnC_3 moieties in alternating $[(\text{CH}_3)_3\text{Sn}]^{\delta+}$ and $[\text{N}_3(\text{CH}_3)_3\text{SnN}_3]^{\delta-}$ environments are bridged through the α -nitrogen atoms of the azide group.

Organic and inorganic derivatives of the azide group exhibit a variety of properties which have made them the subject of continuing interest. While organic azides are of importance in the drug and dye industry, it is among the metal azides that the most subtle variations of bonding and stability occur, thus placing this class of compounds both at the forefront of research in the explosives industry and as model systems for investigation by the structural chemist¹.

Triorganometal(IV) azides are unique insofar as they have relatively high thermal stability and appear to be shock insensitive². Trimethylsilyl- and germyl azides are liquids at room

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temperature and apparently monomeric, while the corresponding azide derivatives of tin and lead are relatively high melting solids (121° and $>200^\circ\text{C}$, decomp., respectively).² Although infrared and Mössbauer studies strongly suggest a polymeric structure for trimethyltin azide,³⁻⁸ the intriguing question of how the azide bridging actually occurs, i.e., through the α -nitrogen only or, as has been suggested,^{3,8,9} through both the α - and γ -nitrogens, remains uncertain. The situation has prompted us to make a preliminary report of the crystal structure of this complex.

Suitable crystals were obtained by slow vacuum sublimation at ca. 70°C . Trimethyltin(IV) azide crystallizes in the orthorhombic space group $\text{Pnc}2$, $a = 8.684(3)$, $b = 11.727(4)$, and $c = 6.612(1)\text{\AA}$, $Z = 4$, $V = 673.35\text{\AA}^3$, $D_{\text{calc}} = 2.03\text{ g cc}^{-3}$. Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at $138\pm 2\text{K}$ and were corrected for Lorentz, polarization and absorption effects.¹⁰ The structure was solved by Patterson and difference Fourier methods. The tin and non-hydrogen light atoms were refined anisotropically and isotropically, respectively, to an R-value of 5.26% for 922 unique reflections or 6.77% for all data (1249 reflections) using a block-diagonal least squares program.

The structure is shown in Figure 1 along with pertinent

bond lengths and angles. The chain polymeric nature of the complex is confirmed, but there are two other noteworthy features associated with the structure. Firstly, bridging is through the α -nitrogen of the azide group at which the chains are bent with an Sn(1)-N(1)-Sn(2) angle of $133.2(4)^\circ$ in an analogous manner to that found in similar species,¹¹ especially trimethyltin chloride¹² and methoxide.¹³ The SnC_3 moieties are eclipsed in the former, but staggered as in our azide in the latter. In trimethyl-¹⁴ and triphenyltin¹⁵ isothiocyanate, on the other hand, the bridging occurs through both nitrogen and sulfur atoms.

Secondly, as a direct consequence of the space group symmetry there are two non-equivalent tin sites, alternate tin atoms making two short [2.290(6)Å] or two long [2.441(6)Å] bonds to nitrogen (see Figure 1). The geometry at each tin is trigonal bipyramidal with the SnC_3 moieties planar, and the more electronegative nitrogen atoms occupying apical positions with an N(1)-Sn-N(1') angle of $175.8(3)^\circ$ associated with the short Sn-N bonds, and an angle of $178.4(3)^\circ$ associated with the long Sn-N bonds. This the only example of an associated organotin polymer in which the chains consist of alternating tin environments.¹¹ This arrangement is probably best described as a combination of trimethyltin(IV) cations and trimethyltin(IV) diazide anions, $\{[(\text{CH}_3)_3\text{Sn}]^{\delta+} [\text{N}_3(\text{CH}_3)_3\text{SnN}_3]^{\delta-}\}_n$, in a one-dimensional array. The tin atoms are not sufficiently different to be distinguished by ^{119m}Sn Mössbauer

spectroscopy.¹⁶ This and other organotin(IV) azides are currently being subjected to solid state tin-119 nmr study.¹⁷

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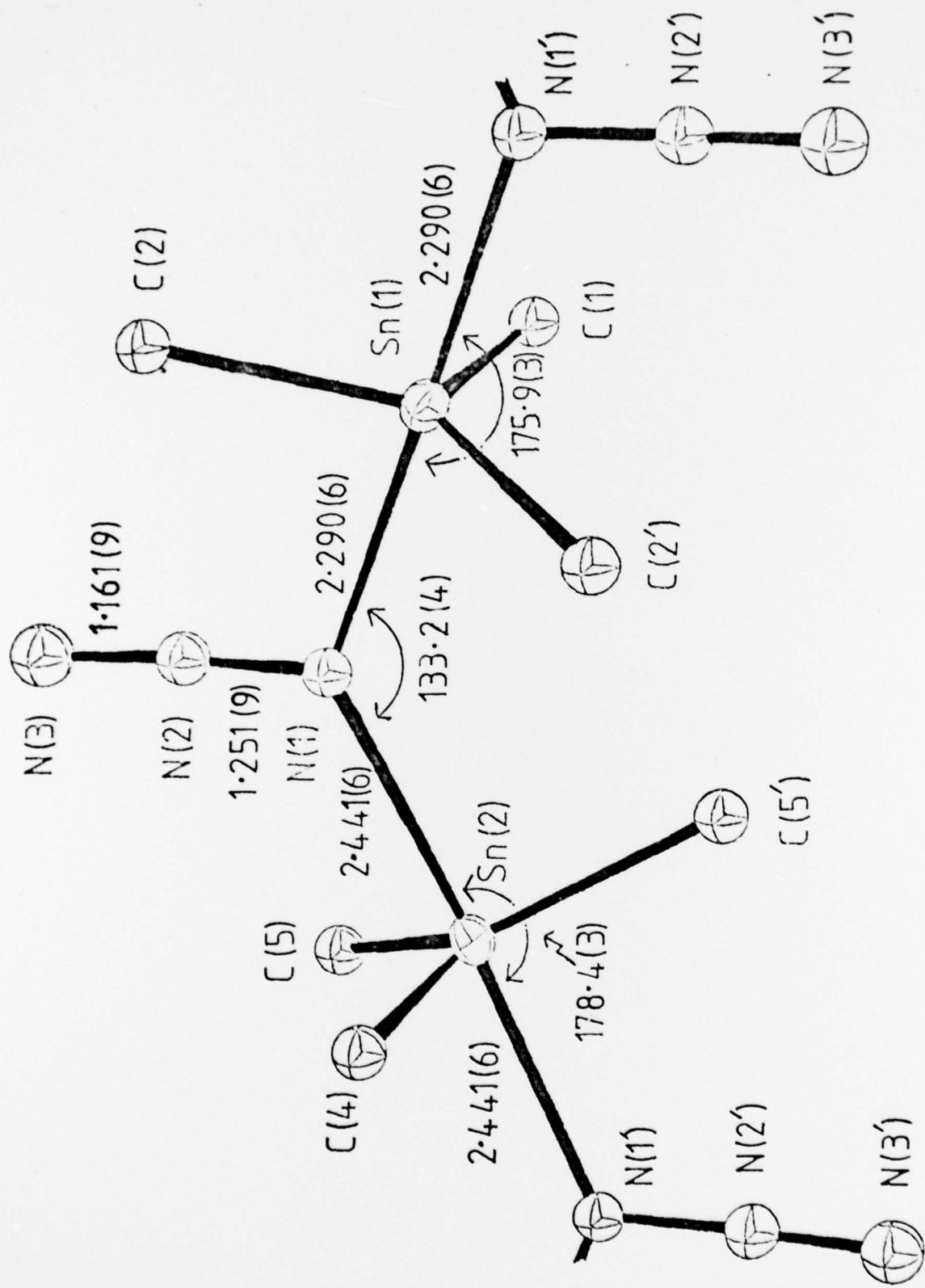
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Figure Caption

Figure 1. A segment of the polymeric structure of trimethyltin azide, showing atomic labelling. Atoms related by a two-fold symmetry along \underline{c} are primed. Atoms in special positions are: Sn(1), C(1)[0,0,z; Wykoff notation:c]; Sn(2), C(4)[1/2,0,z;b]. The remaining atoms are in general positions.



STATEMENT

Our 1978 review of the tin structural literature (ref. 11) reveals many examples of axially-most-electronegative, trigonal bipyramidal triorganotin moieties in associated polymer chains, but the structure of trimethyltin azide is unique in consisting of SnC_3 moieties in alternating $[(\text{CH}_3)_3\text{Sn}]^{\delta+}$ cationic and $[\text{N}_3(\text{CH}_3)_3\text{SnN}_3]^{\delta-}$ anionic environments in a one-dimensional array with the tin atoms bridged at unequal distances by the α -nitrogen atoms of the azide group at which site the chains are bent.

